

INVESTIGATIONS OF THE INFLUENCE OF DIFFERENT FLY ASHES ON CEMENT HYDRATION

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Investigations of physico-chemical properties of three kinds of fly ash and their influence on cement hydration were performed in this work. Thermal analysis, microcalorimetry, infrared absorption and others were used. It was confirmed that the kind of coal and combustion conditions essentially influence physico-chemical properties of fly ash and in consequence influence cement hydration. Investigated fly ashes show in cement system so-called pozzolanic activity. Fly ash from combustion of brown coal in fluidized furnace revealed better activity compared to other investigated ones. This work is an introduction to more extensive investigation of fly ash activation.

Keywords: cement hydration, cement paste, fly ash, pozzolanic activity

Introduction

Among different industrial waste one can distinguish several groups of combustion by-products coming from energy production and waste utilization. There are many types of ashes, which may be classified for the sake of their origin as: fly ash from combustion of hard and brown coal, fly ash of municipal solid waste incineration, rice husk ash, wheat straw ash and others.

Fly ash is a by-product produced in high amounts from the combustion of coal in power plants. For example in 2004 year in Poland about 4 million ton of coal fly ash and 3.7 million ton of mixtures of fly ash and solid waste from limestone methods of desulphurization of waste gases were produced [1].

In many research institutes in the world, works concerning ways of utilization of different types of ash has been undertaken for many years. Fly ash is currently widely applied among other things in cement and cement composite production. However, the analysis of the latest scientific literature shows that investigations concerning their effective utilization are continually topical issues. Research works concerning fly ashes in cement systems are made in several directions in which one may specify the investigation of:

- cement hydration in the presence of different ashes and in changeable conditions (different types of applied cement, water/cement ratio, hardening condition, etc.) whose example are works [2–4];
- influence of ash presence on properties of fresh concrete or mortar cement mixtures and on properties of final composites (for example in works [5, 6]);
- fly ash activation (e.g. [7, 8]);

- utilization possibilities, including influence on physico-chemical processes and properties of materials, of different origin ashes, as: fly ash of municipal solid waste incineration [9, 10], ash from rice husk combustion [11], or fly ash with non-standard properties [12];
- application of ashes as components of binders used for the utilization/solidification of different waste [13].

One of effective methods of fly ash using is their introducing as a substrate in cement production process. Cements with fly ashes are classified according with Polish/European Standard [14] as fly ash Portland cements and are marked as CEM II A and CEM II B (content of fly ash respectively 6–20 and 21–35%). Fly ashes applied with other additives may be components of so called pozzolanic cements (CEM IV) and multicomponent cements (CEM V). Fly ash may be also applied as additive for cement mortar and concrete production on the building site. In this case, fly ash is introduced as replacement of part of the cement or the part of aggregate.

Physico-chemical properties of fly ashes depend on many factors, as: kind of fuel combustion, the kind of furnace, manner of off-gas desulfurization and others, which finally, in different manner, influence their behavior in the cement system. Differences in oxide composition of fly ashes may be the base of their classification. In literature work [15] the classification was proposed as following:

silicate fly ash
($\text{SiO}_2 > 40\%$, $\text{Al}_2\text{O}_3 < 30\%$, $\text{CaO} < 10\%$, $\text{SO}_3 < 4\%$)

aluminate fly ash
($\text{SiO}_2 > 40\%$, $\text{Al}_2\text{O}_3 > 30\%$, $\text{CaO} < 10\%$, $\text{SO}_3 < 3\%$)

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calcium fly ash
(SiO₂>30%, Al₂O₃<30%, CaO>10%, SO₃>3%)

Polish/European Standard [14] divides fly ashes for the sake of the content of CaO in silicate fly ash (marked V) and calcium fly ash (W). In this connection, fly ash in the cement system can reveal pozzolanic or hydraulic properties.

Fly ash in cement paste shows pozzolanic properties, which means that it combines Ca(OH)₂ revealing in cement hydration. As a result, additional amounts of hydrate silicate and aluminate phases are formed. Fly ash pozzolanic activity displays in subsequent hydration days. In initial periods, particles of fly ash are the crystallization centers of hydration products precipitation. Lower initially activity of fly ash explains the phenomenon of reducing of cement composite strength in the early periods [16].

The aim of this work was to determine and compare the physico-chemical properties of three kinds of fly ashes coming from energy industry and investigate a correlation between a kind of ash and its influence on hydrating cement system. These investigations are the first stage of works whose aim will be activation of selected fly ash.

In presented work there are two segments of researches. The first one concerns fly ashes investigation, and the second – their influence on cement hydration.

Experimental

Materials

Experimental work was performed with using of

- Portland cement type CEM I 32.5 R [14],
- three types of fly ash:
 - fly ash from brown coal combustion in fluidized furnace – marked as PF;
 - fly ash from brown coal combustion in conventional furnace (pulverized combustion) – marked as PP;
 - fly ash from hard coal combustion in conventional furnace (pulverized combustion) – marked as PM.

Cement paste preparation

Cement pastes were produced using Portland cement CEM I 32.5 R, fly ash and water. The amounts of fly ash used were 0 (control sample), 10, 20 and 30% of the binder mass (binder=cement+fly ash). The pastes were prepared with constant ratio of water/binder=0.5. Cement and fly ash were firstly mixed together, then water was added and mixed. Cement pastes designed for thermal analysis and IR studies were sealed in poly-

ethylene bags. After appointed time the pastes were crushed and washed with acetone to remove free water and thus stop the hydration reaction. The dried powdered samples were subsequently analysed.

Methods

Fly ash investigations

- In fly ash investigations several methods were used:
- chemical composition was determined by the use of atomic absorption spectrometry on the SOLAR 939 apparatus and by the use of X-ray fluorescence on the Explorer S4 apparatus;
- granulometric composition was determined by the use of sieve analysis – wet screening;
- specific surface was determined from N₂ adsorption isotherms (BET);
- phase composition (crystalline components) – X-ray diffraction by the use of HZG-4C diffractometer (CuK_α radiation);
- thermal analysis (TG, DTG, DTA) were carried out for 9–13 mg samples, with the help of the TA Instruments SDT 2960 thermoanalyser, working up to 1000°C in air atmosphere, at the heating rate of 10°C min⁻¹.
- IR studies were done with help of Mattson FTIR Spectrometer Genesis II in the range of wave numbers from 400 to 4000 cm⁻¹, the samples were prepared as KBr pellets.

Cement pastes investigations

- for thermal analysis (TG, DTG, DTA) TA Instruments SDT 2960 thermoanalyser was used, working in the temperature range up to 1000°C in air atmosphere, at the heating rate of 10°C min⁻¹, the sample mass was carried out for 9–13 mg, investigations were carried out after 3, 7, 28 and 90 days of hydration;
- for the calorimetric measurements a differential BMR calorimeter was used, constructed in the Institute of Physical Chemistry in Warsaw, cement pastes were hydrated in calorimeter at a starting temperature 25°C, the heat evolution curves were registered, and the heat evolved after 24 and 48 h from the beginning of the reaction with water were computed,
- for IR studies Mattson FTIR Spectrometer Genesis II was used (the range of wave numbers 400–4000 cm⁻¹, the samples were prepared as KBr pellets), investigations were carried out after 3 and 90 days of hydration.

Results of investigations of chemical and granulometric compositions of fly ashes as well as of thermal analysis were expressed as percentages in mass.

Results and discussion

Fly ash

The oxide composition of fly ashes (Table 1) shows that PM fly ash is characterized with the biggest total content of SiO_2 (above 50%), the content of Al_2O_3 is comparable for all ashes and amounted 30% (slightly more in case of PP – about 34%). PM fly ash characterizes also the biggest amount of Fe_2O_3 (above 4%). In case of PF fly ash a total content of CaO is several times greater than for the other samples and amounts above 11%, also the amount of SO_3 is the biggest – almost 4%. The analysis of the chemical composition of fly ashes permits their classification for the sake of division proposed in [15] as: PM – silicate fly ash, PP – aluminate fly ash, PF – calcium fly ash (but in case of PM and PF – the amount of Al_2O_3 is critical (30%)).

X-ray diffraction results, which are shown in Fig. 1 and in Table 1, permit the evaluation of fly ash phase composition, i.e. crystalline components. In all fly ashes, the presence of quartz (SiO_2) was identified. Moreover, PP and PM fly ashes include also mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), that formed during coal combustion in high temperatures. In PF and PP samples the

Table 1 Physico-chemical properties of PF, PP and PM fly ash

Property	Fly ashes		
	PF	PP	PM
oxide composition/mass%			
SiO_2	39.4	44.8	51.4
Al_2O_3	30.0	33.8	30.0
Fe_2O_3	2.16	2.30	4.19
CaO	11.64	3.75	1.33
MgO	1.40	1.37	1.41
SO_3	3.75	0.94	0.61
Na_2O	1.93	1.98	0.61
K_2O	1.40	1.60	2.83
P_2O_5	0.13	0.12	0.63
phase composition*			
SiO_2 (quartz)	+	+	+
$\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite)		+	+
CaSO_4 (anhydrite)	+	+	
CaO (calcium oxide)	+	+	
Fe_2O_3 (hematite)	+		
$\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite)	+		
Density/ g cm^{-3}	2.440	2.017	2.023
Specific surface/ $\text{m}^2 \text{g}^{-1}$	8.3	5.9	4.6
Loss of ignition**/mass%	1.9	1.3	3.5

*mark (+) means, that presence of a component was confirmed by X-ray analysis

**total mass loss in temperature range up to 1000°C (thermal analysis – TG results)

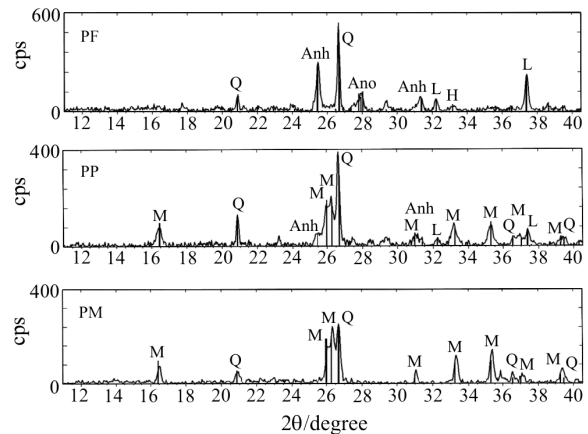


Fig. 1 X-ray patterns of PF, PP and PM samples; Q – quartz, Anh – anhydrite, Ano – anorthite, L – lime, H – hematite, M – mullite

presence of anhydrite (CaSO_4) and calcium oxide (CaO) was found. Besides, mentioned components in the PF sample the presence of hematite (Fe_2O_3) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) was found.

Obtained results of fly ash chemical compositions were partially confirmed in IR absorption studies (Fig. 2). The main absorption band is an intensive band with a maximum at about 1100 cm^{-1} , which can be attributed to the stretching vibrations of Si–O [17]. Broad band with a maximum at about 3450 cm^{-1} , observed for PF and PM samples, as well as weak band at about 1640 cm^{-1} (for PF) are connected with moisture in samples. The presence of very weak band at 3640 cm^{-1} for PF fly ash may suggest small content of $\text{Ca}(\text{OH})_2$.

Thermal analysis, whose results (TG and DTG curves) are presented in Fig. 3, permits determining ignition losses, which for investigated fly ashes were in the range of 1.3–3.5%. The mass loss in temperature range from 500 to 700°C is connected probably with the combustion of coal in samples.

Granulometric composition results presented in Fig. 4 show that investigated fly ashes are very fine-grained materials. Main grain fraction were

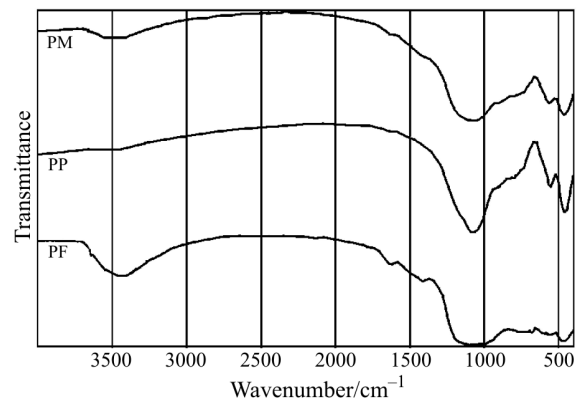


Fig. 2 IR spectra of PF, PP and PM samples

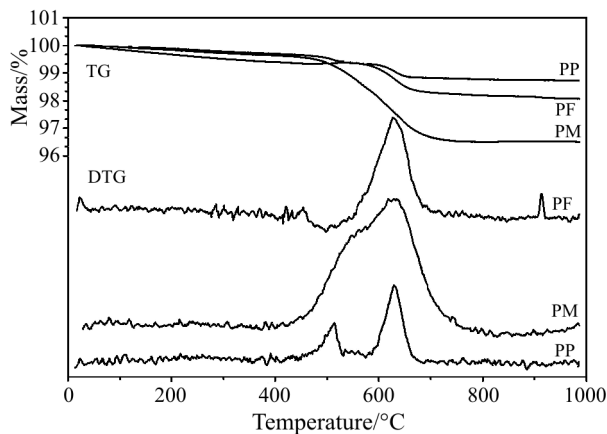


Fig. 3 TG and DTG curves for PF, PP and PM samples

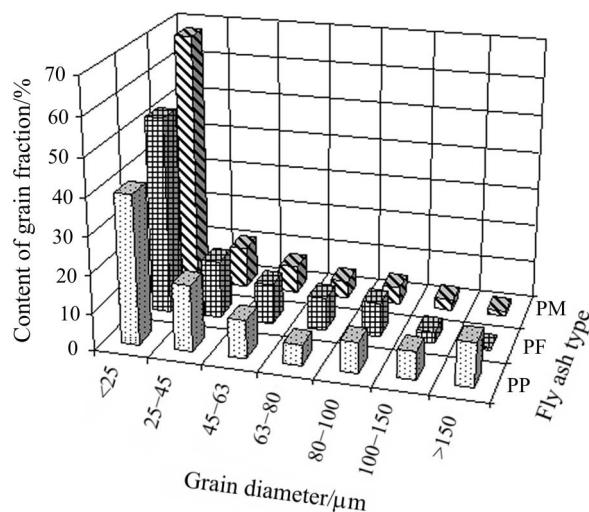


Fig. 4 Grain size distribution of PF, PP and PM samples

grains with diameter below 25 µm. Specific surface of fly ash (Table 1) is the biggest for PF sample, which means that this material is the most porous.

These investigations have confirmed that fly ashes from different sources, varying in kind of combustion material and combustion conditions, show different physico-chemical properties. Taking it into consideration, one should expect, that they will influence hydration processes of cement differently. Considering chemical composition of fly ashes one may state that calcium silicate hydrates of the type C-S-H as well as aluminates and sulphoaluminates will be the products of pozzolanic reactions. Better activity will be shown by fly ashes containing higher amounts of amorphous forms comparing to those containing higher amounts of crystalline less active phases. In case of PF fly ash higher content of sulphates may cause arising of bigger amounts of ettringite. This phenomenon may be unfavorable if expansive ettringite will be form after cement hardening, causing microtensions. The so-called delayed formation and crystallization of ettringite may be

accompanied by expansion of cement paste and in consequence durability of composite may decrease. The phenomenon of delayed ettringite formation in cement pastes admixed with fly ash was observed by the authors of work [2]. In case of PF and PP fly ashes the presence of CaSO₄ and CaO in their composition may be important. The presence of CaSO₄ in hydrating cement system may influence setting time. From the other hand, CaSO₄ can act as fly ash activator accelerating a pozzolanic reaction. CaO can also show active influence on the pozzolanic reaction. Both these compounds are applied as chemical activators, as in works [8, 18], however the mechanism of their acting is different.

Analyzing fly ash grain size one may suppose that materials with smaller grains may show better activity in the cement system comparing to those with coarse grains.

But one cannot forget that fly ash activity depends on chemical composition, phase composition, granulometric composition and also on other factors, as: temperature, curing conditions, water to cement ratio and others.

Cement pastes

Thermal analysis

Examples of obtained results of thermal studies are presented in Figs 5 and 6 (TG, DTG and DTA curves). They are typical for cement pastes. There are three main mass losses on TG curves:

- up to temperature about 450°C – endothermic dehydration of hydrated calcium silicates (C-S-H phase), hydrated calcium aluminates and sulphoaluminates (also ettringite) – in this work this mass loss is marked as Δm 1,
- from about 450 to about 480°C – endothermic decomposition of Ca(OH)₂ – Δm 2,
- above 500°C – decomposition of carbonates – Δm 3

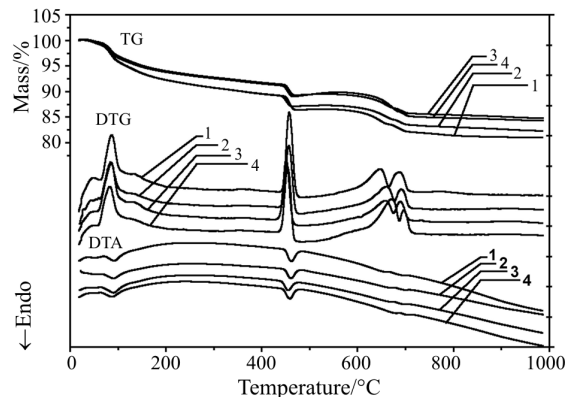


Fig. 5 TG, DTG and DTA curves for cement pastes after 3 days of hydration 1 – control cement paste (0% of fly ash), 2 – 30% of PF, 3 – 30% of PP, 4 – 30% of PM

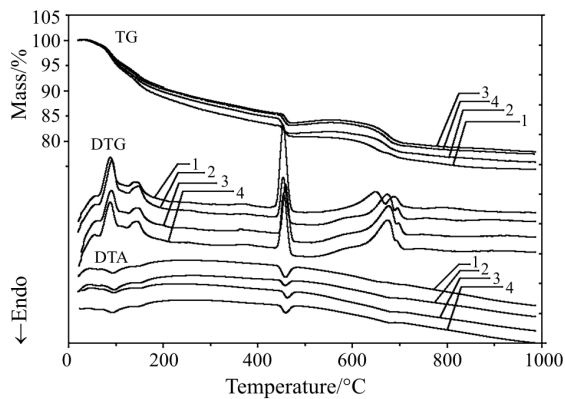


Fig. 6 TG, DTG and DTA curves for cement pastes after 90 days of hydration 1 – control cement paste (0% of fly ash), 2 – 30% of PF, 3 – 30% of PP, 4 – 30% of PM

Differences in the values of individual mass losses show differences in quantity composition of cement pastes depending on presence, amount and kind of fly ash and also on hydration time.

In Fig. 7 the comparison of quantities of $\Delta m 1$ for cement pastes are presented. It is assumed that quantity of $\Delta m 1$ represents the amount of water combined in hydrates of C–S–H type and of other kinds. Moreover most of hydrates undergo dehydration in this temperature range. This approach is only an approximation, because some hydrates can undergo dehydration also in temperatures above 500°C and from about 300°C some components of cement paste may undergo decarbonation [19, 20]. Moreover, introducing pozzolanic additives to the cement system causes arising of hydrates of varying water content (different CaO/SiO₂ and H₂O/SiO₂ ratios) than in case of neat cement. That is why determining of so-called chemically bound water in hydrates ($\Delta m 1$ in this work) and also non-evaporable water (defined as mass loss during heating of samples in temperatures from 105 to 1000°C) does not allow determining exactly the degree of hydration [19, 21]. In spite of some limitations, determination of quantity of water bounded in cement

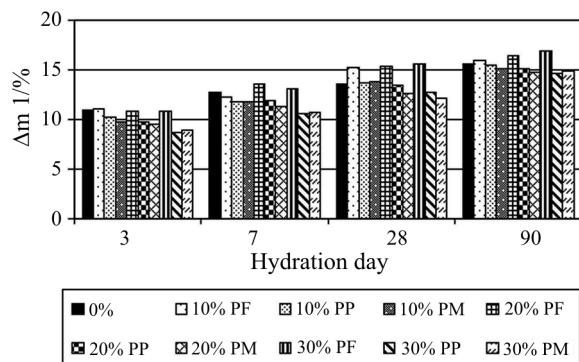


Fig. 7 $\Delta m 1$ values for cement pastes in different days of hydration

pastes by the use of thermal analysis is often applied. From the data presented in Fig. 7 it can be seen that quantities of $\Delta m 1$ increase with time, which is connected with the hydration progress. In case of cement pastes with PP and PM addition values of $\Delta m 1$ in initial hydration days are lower than for control cement paste, which suggests lower fly ash activity in those periods. But in case of PP-cement paste starting from the 3rd hydration day, and in case of PM-cement paste – from the 7th hydration day, observed reducing of $\Delta m 1$ values is lower than percentage of fly ash content. In subsequent hydration days, $\Delta m 1$ values of fly ashes (PP and PM) cement pastes and of control sample are similar. Probably these fly ashes show lower activity in initial hydration days. Reducing of $\Delta m 1$ in this period is caused by ‘dilution’ the binder by less active component than cement. In consequence decreased amounts of C–S–H and other products are formed. In initial periods fly ash grains probably act as nucleation centers for precipitation of cement hydration products. Rising to the nearly equal level of $\Delta m 1$ both by fly ash cement paste and control cement paste may be the consequence of the pozzolanic reaction occurring and forming of C–S–H and hydrates aluminates in this reaction.

In the case of cement pastes with PF fly ash addition as early as in the 3rd hydration day $\Delta m 1$ values are close to this obtained for control sample, and in subsequent days they exceed it slightly. It suggests better activity of PF fly ash comparing with PP and PM fly ashes. As an effect larger amounts of water is bounded in hydrates.

Changes of $\Delta m 2$ values for cement pastes are presented in Fig. 8. Value of $\Delta m 2$ is connected with Ca(OH)₂ decomposition and is proportional to Ca(OH)₂ content in the sample (knowing $\Delta m 2$ value one can, in simple manner, estimate Ca(OH)₂ content in sample basing on stoichiometry of decomposition reaction; this method is one of the best among various methods of estimation of pozzolanic activity [19, 22]). From the presented data one can see, that in each case,

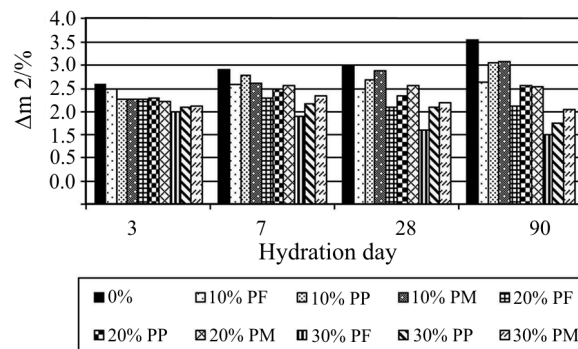


Fig. 8 $\Delta m 2$ values for cement pastes in different days of hydration

introducing fly ash to the cement paste causes decreasing of Δm_2 (thus also $\text{Ca}(\text{OH})_2$ content). However, in initial days of hydration decreasing of Δm_2 values is proportional to amounts of introduced fly ash and probably is not a result of a pozzolanic reaction occurring but of partially replacement of cement with the material of lower activity. In subsequent periods, decrease of Δm_2 is greater than the percentage of additive in systems in comparison to values obtained for control cement paste. Thus, obtained results confirmed low initial activity of fly ashes and disclosing of pozzolanic properties in subsequent days. Comparing Δm_2 values obtained for cement pastes with different fly ash additives one can state that PF fly ash in bigger degree causes $\text{Ca}(\text{OH})_2$ decreasing than the others. Thereby, PF shows better pozzolanic activity. PF fly ash probably also shows hydraulic properties for the sake of the biggest CaO content. Pozzolanic activity of PP and PM fly ashes seems to be similar.

Calorimetric measurements

The heat evolution curves and heat-evolved values are presented in Figs 9 and 10, respectively.

Registered curves of heat evolution are typical for cement pastes. After the first exothermal effect connected with wetting and dissolving of components, the so-called induction period (heat evolution is stopped) follows, and then repeated growing of heat release takes place which is caused by crystallization of cement hydration products, especially silicate phases. Replacement of the part of cement with fly ash modifies the heat evolution, thus it influences initial periods of cement hydration. This influence is depended on the kind and the amount of fly ash.

Fly ash in amount of 10% influences the heat evolution rate only in slight degree. Calorimetric curves of cement pastes with fly ash addition are almost identical as curves for control cement paste, but in case of PM and PP fly ash inconsiderable retardation is observed and in case of PF fly ash – small acceleration of cement hydration. In case of larger amounts of fly ash, obtained curves of heat release are more flat and extended in time comparing with microcalorimetric curve obtained for control cement paste. Induction period is also elongated. This means that the hydration products form slowly. Observed changes are the most visible for 30% of PM and PP fly ash.

For cement pastes with PF fly ash addition the reducing of the amount of heat released is not observed. However in case of cement pastes with PM and PP fly ash the amount of heat released decreases as the amount of additive increases. It proves more active effect of PF fly ash than PM and PP.

Obtained results confirm information included in literature work [23], in which the author shows that

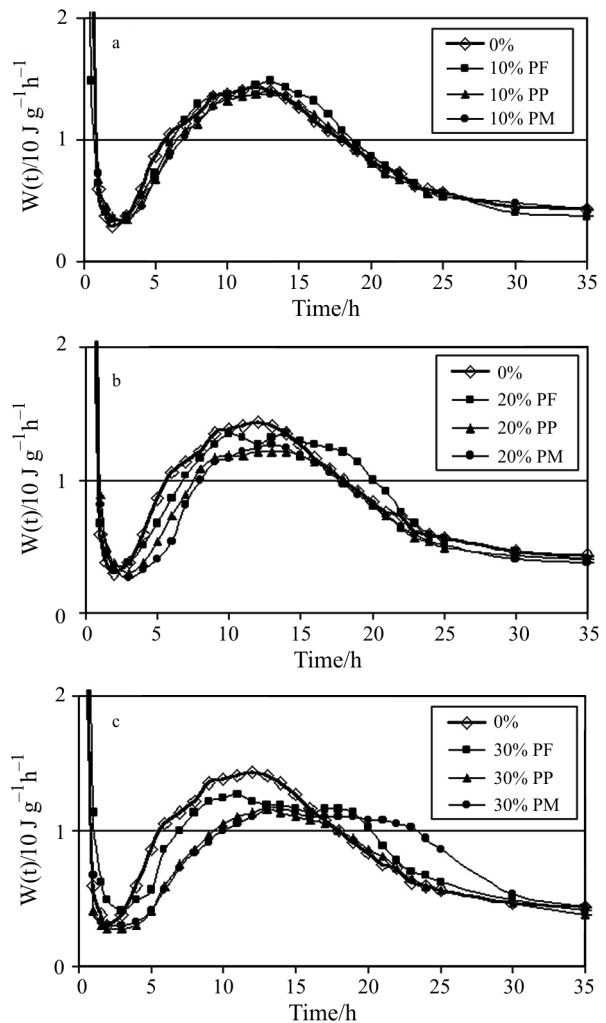


Fig. 9 Heat evolution curves for cement pastes with fly ash addition (a – 10, b – 20 and c – 30%)

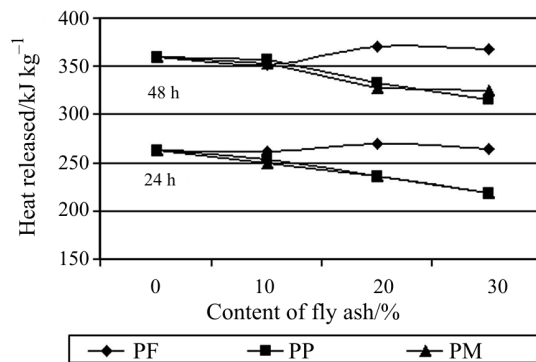


Fig. 10 Heat evolved within 24 and 72 h of hydration

heat evolution rate decreases with the amount of fly ash increase and it is accompanied with delayed and extended in time forming of silicate phases. The reduction of amount of heat released after 24 and 48 h of hydration of cement pastes with PP and PM fly ash confirms tendency characteristic for fly ash cements.

For these cements in initial hydration period moderate kinetics of heat evolved during setting and hardening processes is stated. It was proved by the authors of [24], who investigated the properties of fly ash cement CEM II/B V 32.5 R.

Infrared absorption

Examples of the IR results obtained for cement pastes on 3rd and 90th hydration days are presented in Figs 11 and 12. The shape of infrared spectra is typical for cement pastes. There are several groups of characteristic bands. An intense, broad band with a maximum at about 3400 cm⁻¹ and a weak band at about 1650 cm⁻¹ may be accounted to the presence of water in the material. According to interpretation given in a book [25] the region of 3000–3700 cm⁻¹ may also contain absorption bands due to the presence of ettringite (3420 and a weaker one at 3635 cm⁻¹) and of monosulphate (3100, 3500 (broad), 3540 and 3675 cm⁻¹) and also of Ca(OH)₂ (a peak about 3640 cm⁻¹). The intensive absorption band at about

970 cm⁻¹ is due to the formation of the C–S–H phase [25]. Absorption bands due to the presence of carbonates are observed at about 1440 cm⁻¹. Observed in initial hydration periods peak at about 1105 cm⁻¹ probably comes from S–O vibrations in sulphates (gypsum). At subsequent hydration period the intensity of this peak decreases as a consequence of chemical reactions occurring.

From the point of view of investigations presented in this work the presence and intensity of Ca(OH)₂ peak was especially important. It has been stated that in initial hydration days intensity of Ca(OH)₂ band is similar to that obtained for control cement pastes. In subsequent hydration period the intensity of Ca(OH)₂ band is visibly decreased for fly ash cement pastes compared to the control one. It confirms that pozzolanic activity of fly ash displays in subsequent hydration days. Unfortunately, results obtained by this method do not enable accurate comparison for pozzolanic activity of investigated different types of fly ash.

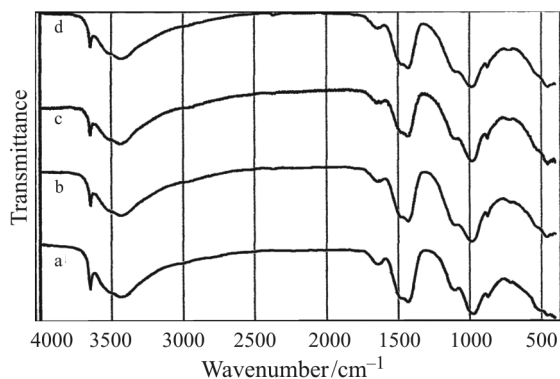


Fig. 11 IR spectra of cement pastes on 3rd day of hydration
a – control cement paste (0% of fly ash), b – 30% of PF, c – 30% of PP, d – 30% of PM

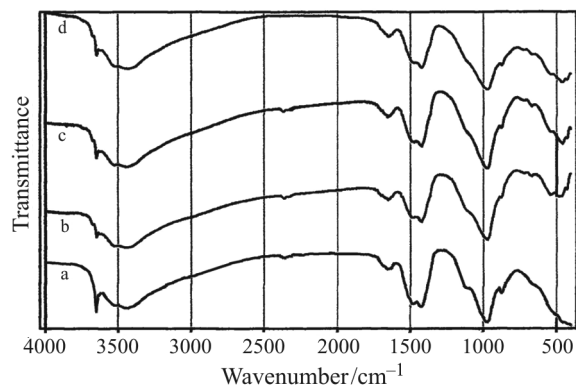


Fig. 12 IR spectra of cement pastes on 90th day of hydration
a – control cement paste (0% of fly ash), b – 30% of PF, c – 30% of PP, d – 30% of PM

Conclusions

Performed investigations confirm that fly ash from different sources, varying in kind of coal combusted, kind of furnace used and thus combustion conditions, show different physico-chemical properties, as chemical composition, granulation and morphology of grains. Thereby, the influence of such fly ash on cement hydration is different.

Investigated fly ash samples show pozzolanic properties, which was proved by thermal analysis and infrared absorption studies. The amount of Ca(OH)₂ in cement pastes was reduced in case of cement pastes with fly ash addition compared with control one. It was also confirmed that pozzolanic properties of ash reveal rather in subsequent hydration days (especially in case of PP and PM fly ash). PF fly ash shows better pozzolanic activity comparing with investigated other ones.

Better activity of PF fly ash was proved also in microcalorimetric investigations. In case of cement pastes with PF addition the reduction of heat released was not observed. Microcalorimetric curve for 10% PF addition showed certain acceleration of hydration. PM and PP fly ashes show effect of somewhat retardation of cement hydration rate, which is especially visible if their larger amounts are considered.

Performed investigations confirm the possibility of fly ash utilization in the cement system. It was important from the point of view of environment protection (waste removing) and also from the point of view of energy saving (smaller amounts of cement used). However different influence of PF, PP and PM fly

ashes on cement hydration suggests also different influence on properties of cement mortars and concretes.

Obtained results encourage continuing research works. A continuation of this work will be fly ash activation investigation.

Acknowledgements

The authors wish to appreciate the contribution of Prof. Wiesława Nocuń-Wczelik in performing calorimetric studies and in remarks on interpretation of the results.

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Received: September 5, 2005

Accepted: October 5, 2005

OnlineFirst: May 16, 2006

DOI: 10.1007/s10673-005-7136-7